UNITED STATES PATENT AND TRADEMARK OFFICE

I, Charles Edward SITCH BA,

Deputy Managing Director of RWS Group Ltd UK Translation Division, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England declare;

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.

2. That the translator responsible for the attached translation is well acquainted with the French and English languages.

3. That the attached is, to the best of RWS Group Ltd knowledge and belief, a true translation into the English language of the specification in French filed with the application for a patent in the U.S.A. on

under the number

4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.

For and on behalf of RWS Group Ltd

The 17th day of September 2004

FRENCH REPUBLIC

INPI
INSTITUT NATIONAL DE LA PROPRIETE INDUSTRIELLE

PATENT

UTILITY CERTIFICATE – CERTIFICATE OF ADDITION

OFFICIAL COPY

The Director-General of the Institut National de la Propriété Industrielle certifies that the attached document is a true copy of an application for industrial property titleright filed at the Institute.

Drawn up in Paris, **10 SEPT. 2004**

On behalf of the Director-General of the
Institut National de la Propriété Industrielle
The Patent Department Head

[signature]

Martine PLANCHE

INSTITUT NATIONAL DE LA PROPRIETE INDUSTRIELLE
REGISTERED OFFICE
26 bis, rue de Saint Petersbourg
75800 PARIS Cédex 08
Telephone: 33 (0)1 53 04 53 04
Fax: 33 (0)1 53 04 45 23
www.inpi.fr

COMPOSITION FOR THE OXIDATION DYEING OF KERATIN FIBERS, AND DYEING PROCESS USING THIS COMPOSITION

The invention relates to a composition for the oxidation dyeing of keratin fibers, and in particular of human keratin fibers such as the hair, comprising, in a medium that is suitable for dyeing, at least one heterocyclic oxidation dye and at least one laccase-type enzyme, and also to the dyeing process using this composition.

It is known practice to dye keratin fibers, and in particular human hair, with dye compositions containing one or more oxidation dye precursors, in particular ortho- or para-phenylenediamines, ortho- or para-aminophenols, and heterocyclic bases, which are generally known as oxidation bases. These oxidation dyes (oxidation bases) are colorless or weakly colored compounds which, when combined with oxidizing products, can give rise to colored compounds and dyes by a process of oxidative condensation.

It is also known that the shades obtained with these oxidation bases can be varied by combining them with couplers or coloration modifiers, the latter being chosen in particular from aromatic meta-diamines, meta-aminophenols, meta-diphenols and certain heterocyclic compounds.

The variety of molecules used as oxidation bases and couplers allows a wide range of colors to be obtained.

The so-called "permanent" coloration obtained by means of these oxidation dyes should moreover satisfy a

certain number of requirements. Thus, it should have no toxicological drawbacks, it should allow shades to be obtained in the desired intensity and it should have good staying power with respect to external agents (light, bad weather, washing, permanent-waving, perspiration or rubbing).

The dyes should also allow gray hair to be covered and, finally, they should be as unselective as possible, i.e. they should allow only the smallest possible differences in coloration to be obtained along the same keratin fiber, which may indeed be differently sensitized (i.e. damaged) between its end and its root.

The oxidation dyeing of keratin fibers is generally carried out in alkaline medium, in the presence of hydrogen peroxide. However, the use of alkaline media in the presence of hydrogen peroxide has the drawback of resulting in substantial degradation of the fibers, and also decolorization of the keratin fibers, which is not always desirable.

The oxidation dyeing of keratin fibers can also be carried out using oxidizing systems other than hydrogen peroxide, such as enzymatic systems. Thus, it has already been proposed in US patent 3 251 742 and patent applications FR-A-2 112 549, FR-A-2 694 018, EP-A-0 504 005, WO 95/07988, WO 95/33836, WO 95/33837, WO 96/00290, WO 97/19998 and WO 97/19999, to dye keratin fibers with compositions comprising at least one oxidation dye, or at least one melanin precursor, in combination with laccase-type enzymes, said compositions being placed in contact with atmospheric oxygen. Although these dye formulations are used under

conditions that do not result in the degradation of keratin fibers comparable to that generated by dyes used in the presence of hydrogen peroxide, they lead to colorations that are still insufficient both in terms of the homogeneity of the color distributed along the fiber (unison) and in terms of the chromaticity (luminosity) and dyeing power.

The Applicant has now discovered that it is possible to obtain novel dyes that are capable of giving more intense colorations without generating any significant degradation of keratin fibers, and that are relatively unselective and stand up well to the various attacking factors to which the fibers may be subjected, by combining at least one suitably selected heterocyclic oxidation dye (oxidation base and/or coupler) and at least one laccase-type enzyme.

This discovery forms the basis of the present invention.

A first subject of the invention is thus a ready-to-use composition for the oxidation dyeing of keratin fibers, and in particular of human keratin fibers such as the hair, characterized in that it comprises, in a medium that is suitable for dyeing,

- at least one oxidation dye chosen from heterocyclic oxidation bases and heterocyclic couplers, and
- at least one laccase-type enzyme,

said composition being free of heterocyclic coupler chosen from indole, indoline, monocyclic pyridine and phenazine compounds.

The ready-to-use dye composition in accordance with the

invention leads to intense, chromatic colorations. The colorations obtained with the ready-to-use dye composition in accordance with the invention moreover show little selectivity and excellent properties of resistance both with respect to atmospheric agents such as light and bad weather and with respect to perspiration and the various treatments to which hair may be subjected (washing, permanent-waving).

A subject of the invention is also a process for the oxidation dyeing of keratin fibers using this ready-to-use dye composition.

The laccase(s) used in the ready-to-use dye composition in accordance with the invention can be chosen in particular from laccases of plant, animal or microbial origin or obtained by biotechnology.

Among the laccases of plant origin that can be used according to the invention, mention may be made of the laccases produced by plants that carry out chlorophyll synthesis, such as those mentioned in patent application FR-A-2 694 018.

Mention may be made in particular of the laccases extracted from Anacardiacea plants, from Podocarpacea plants, from Rosmarinus off., from Solanum tuberosum, from Iris sp., from Coffea sp., from Daucus carrota, from Vinca minor, from Persea americana, from Catharanthus roseus, from Musa sp., from Malus pumila, from Gingko biloba, and from Monotropa hypopithys (Indian pipe).

Among the laccases of microbial (in particular fungal)

origin, or obtained by biotechnology, which can be used according to the invention, mention may be made of the laccases of Polyporus versicolor, of Rhizoctonia praticola and of Rhus vernicifera as described, for example, in patent applications FR-A-2 112 549 and EP-A-504 005; the laccases described in patent applications WO 95/07988, WO 95/33836, WO 95/33837, WO 96/00290, WO 97/19998 and WO 97/19999, the content of which forms an integral part of the present description, such as, for example, the laccases of Scytalidium, of Polyporus pinsitus, of Myceliophthora thermophila, of Rhizoctonia solani, of Pyricularia oryzae, and variants thereof.

Laccases of microbial origin or those obtained by biotechnology will more preferably be chosen.

The enzymatic activity of the laccases used in accordance with the invention can be defined by the oxidation of syringaldazine under aerobic conditions as indicated in application WO 97/37633. One Lacu unit corresponds to the amount of enzyme that catalyzes the conversion of 1 mmol of syringaldazine per minute at a pH of 5.5 and at a temperature of 30°C. One U unit corresponds to the amount of enzyme that produces an absorbance delta of 0.001 per minute at a wavelength of 530 nm, using syringaldazine as substrate, at 30°C and at a pH of 6.5.

The amount of laccase(s) present in the ready-to-use dye composition in accordance with the invention will vary as a function of the nature of the laccase(s) used. Preferably, the amount of laccase(s) is between 0.5 and 200 Lacu approximately (i.e. between 10 000 and

4×10^6 U units approximately) per 100 g of dye composition.

Among the heterocyclic oxidation bases that can be used in the ready-to-use dye composition according to the invention, mention may be made in particular of pyrimidine derivatives and pyrazole derivatives, and the addition salts thereof with an acid.

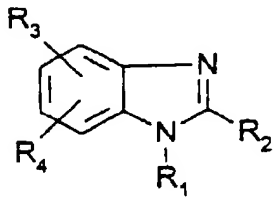
Among the pyrimidine derivatives that may be mentioned more particularly are the compounds described, for example, in German patent DE 2 359 399 or Japanese patents JP 88-169 571 and JP 91-333 495, such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, and the addition salts thereof with an acid and pyrazolopyrimidine derivatives such as pyrazolo[1,5-a]pyrimidine-3,7-diamine, 2-methylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,5-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, pyrazolo[1,5-a]pyrimidine-3,5-diamine, 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine, 3-aminopyrazolo[1,5-a]pyrimidin-7-ol, 3-amino-5-methylpyrazolo[1,5-a]pyrimidin-7-ol, 3-aminopyrazolo[1,5-a]pyrimidin-5-ol, 2-(3-aminopyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol, 3-amino-7-β-hydroxyethylamino-5-methylpyrazolo[1,5-a]pyrimidine, 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol, 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)-(2-hydroxyethyl)amino]ethanol, 2-[(7-aminopyrazolo[1,5-a]pyrimidin-3-yl)-(2-hydroxyethyl)amino]ethanol, 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine and 2,5,N7,N7-tetramethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, and the addition salts thereof and the tautomeric forms thereof, when a tautomeric equilibrium exists.

Among the pyrazole derivatives that may be mentioned more particularly are the compounds described in patents or patent applications DE 3 843 892, DE 4 133 957, DE 4 234 886, DE 4 234 887, FR 2 733 749, FR 2 735 685, WO 94/08969 and WO 94/08970, such as 4,5-diaminopyrazole, 4,5-diamino-1-methylpyrazole, 1-benzyl-4,5-diaminopyrazole, 3,4-diaminopyrazole, 1-benzyl-4,5-diamino-3-methylpyrazole, 4-amino-1,3-dimethyl-5-hydrazinopyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-diamino-1-tert-butyl-3-methylpyrazole, 4,5-diamino-3-tert-butyl-1-methylpyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole, 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole, 4,5-diamino-3-hydroxymethyl-1-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole and 4,5-diamino-3-methyl-1-isopropylpyrazole, and the addition salts thereof with an acid.

Among the heterocyclic couplers that can be used in the ready-to-use dye composition in accordance with the invention, mention may be made in particular of benzimidazole derivatives, benzomorpholine derivatives, sesamol derivatives, pyrazoloazole derivatives, pyrroloazole derivatives, imidazoloazole derivatives, pyrazolopyrimidine derivatives, pyrazoline-3,5-dione derivatives, pyrrolo[3,2-d]oxazoline derivatives, pyrazolo[3,4-d]thiazole derivatives, thiazoloazole S-oxide derivatives and thiazoloazole S,S-dioxide derivatives, and the addition salts thereof with an acid.

Among the benzimidazole derivatives that can be used as heterocyclic couplers in the dye composition in accordance with the invention, mention may be made more

particularly of the compounds of formula (I) below, and the addition salts thereof with an acid:



(I)

in which:

R_1 represents a hydrogen atom or a C_1-C_4 alkyl radical,

R_2 represents a hydrogen atom or a C_1-C_4 alkyl or phenyl radical,

R_3 represents a hydroxyl, amino or methoxy radical,

R_4 represents a hydrogen atom or a hydroxyl, methoxy or C_1-C_4 alkyl radical;

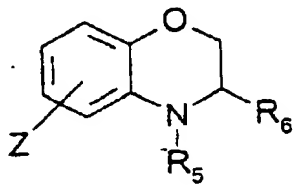
with the proviso that:

- when R_3 denotes an amino radical, then it occupies position 4,
- when R_3 occupies position 4, then R_4 occupies position 7,
- when R_3 occupies position 5, then R_4 occupies position 6.

Among the benzimidazole derivatives of formula (I) above that may be mentioned more particularly are 4-hydroxybenzimidazole, 4-aminobenzimidazole, 4-hydroxy-7-methylbenzimidazole, 4-hydroxy-2-methylbenzimidazole, 1-butyl-4-hydroxybenzimidazole, 4-amino-2-methylbenzimidazole, 5,6-dihydroxybenzimidazole, 5-hydroxy-6-methoxybenzimidazole, 4,7-dihydroxybenzimidazole, 4,7-dihydroxy-1-methylbenzimidazole, 4,7-dimethoxybenzimidazole, 5,6-dihydroxy-1-methylbenzimidazole, 5,6-dihydroxy-2-methylbenzimidazole and 5,6-dimethoxybenzimidazole, and the addition salts thereof with an acid.

Among the benzomorpholine derivatives that can be used

as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds of formula (II) below, and the addition salts thereof with an acid:



(II)

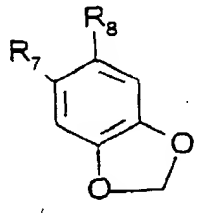
in which:

R_5 and R_6, which may be identical or different, represent a hydrogen atom or a C_1-C_4 alkyl radical,

Z represents a hydroxyl or amino radical.

Among the benzomorpholine derivatives of formula (II) above that may be mentioned more particularly are 6-hydroxy-1,4-benzomorpholine, N-methyl-6-hydroxy-1,4-benzomorpholine and 6-amino-1,4-benzomorpholine, and the addition salts thereof with an acid.

Among the sesamol derivatives that can be used as heterocyclic couplers in the ready-to-use dye composition, mention may be made more particularly of the compounds of formula (III) below, and the addition salts thereof with an acid:



(III)

in which:

R_7 denotes a hydroxyl, amino, (C_1-C_4)alkylamino, monohydroxy(C_1-C_4)alkylamino or polyhydroxy(C_2-C_4)alkylamino radical,

R_8 denotes a hydrogen or halogen atom or a C_1-C_4 alkoxy radical.

Among the sesamol derivatives of formula (III) above that may be mentioned more particularly are 2-bromo-4,5-methylenedioxyphenol, 2-methoxy-4,5-methylenedioxyaniline and 2-(β-hydroxyethyl)amino-4,5-methylenedioxybenzene, and the addition salts thereof with an acid.

Among the pyrazoloazole derivatives that can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in the following patents and patent applications: FR 2 075 583, EP-A-119 860, EP-A-285 274, EP-A-244 160, EP-A-578 248, GB 1 458 377, US 3 227 554, US 3 419 391, US 3 061 432, US 4 500 630, US 3 725 067, US 3 926 631, US 5 457 210, JP 84/99437, JP 83/42045, JP 84/162548, JP 84/171956, JP 85/33552, JP 85/43659, JP 85/172982, JP 85/190779 and also in the following publications: Chem. Ber. 32, 797 (1899), Chem. Ber. 89, 2550, (1956), J. Chem. Soc. Perkin trans 1, 2047, (1977), J. Prakt. Chem., 320, 533, (1978); the teachings of which form an integral part of the present patent application.

Pyrazoloazole derivatives that may be mentioned most particularly are:

- 2-methylpyrazolo[1,5-b]-1,2,4-triazole,
- 2-ethylpyrazolo[1,5-b]-1,2,4-triazole,
- 2-isopropylpyrazolo[1,5-b]-1,2,4-triazole,
- 2-phenylpyrazolo[1,5-b]-1,2,4-triazole,
- 2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole,
- 7-chloro-2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole,

- 3,6-dimethylpyrazolo[3,2-c]-1,2,4-triazole,
- 6-phenyl-3-methylthiopyrazolo[3,2-c]-1,2,4-triazole,
- 6-aminopyrazolo[1,5-a]benzimidazole,

and the addition salts thereof with an acid.

Among the pyrroloazole derivatives that can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in the following patent applications and patents: US 5 256 526, EP-A-557 851, EP-A-578 248, EP-A-518 238, EP-A-456 226, EP-A-488 909, EP-A-488 248, and in the following publications:

- D.R. Liljegren Ber. 1964, 3436;
- E.J. Browne, J.C.S., 1962, 5149;
- P. Magnus, J.A.C.S., 1990, 112, 2465;
- P. Magnus, J.A.C.S., 1987, 109, 2711;
- Angew. Chem. 1960, 72, 956;
- and Rec. Trav. Chim. 1961, 80, 1075; the teachings of which form an integral part of the present patent application.

Pyrroloazole derivatives that may be mentioned most particularly are:

- 5-cyano-4-ethoxycarbonyl-8-methylpyrrolo[1,2-b]-1,2,4-triazole,
- 5-cyano-8-methyl-4-phenylpyrrolo[1,2-b]-1,2,4-triazole,
- 7-amido-6-ethoxycarbonylpyrrolo[1,2-a]benzimidazole,

and the addition salts thereof with an acid.

Among the imidazoloazole derivatives that can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention

may be made more particularly of the compounds described in the following patent applications and patents: US 5 441 863; JP 62-279 337; JP 06-236 011 and JP 07-092 632, the teachings of which form an integral part of the present patent application.

Imidazoloazole derivatives that may be mentioned most particularly are:
- 7,8-dicyanoimidazolo[3,2-a]imidazole,
- 7,8-dicyano-4-methylimidazolo[3,2-a]imidazole,
and the addition salts thereof with an acid.

Among the pyrazolopyrimidine derivatives that can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in the following patent application: EP-A-304 001, the teaching of which forms an integral part of the present patent application.

Pyrazolopyrimidine derivatives that may be mentioned most particularly are:
- pyrazolo[1,5-a]pyrimidin-7-one,
- 2,5-dimethylpyrazolo[1,5-a]pyrimidin-7-one,
- 2-methyl-6-ethoxycarbonylpyrazolo[1,5-a]pyrimidin-7-one,
- 2-methyl-5-methoxymethylpyrazolo[1,5-a]pyrimidin-7-one,
- 2-tert-butyl-5-trifluoromethylpyrazolo[1,5-a]pyrimidin-7-one,
- 2,7-dimethylpyrazolo[1,5-a]pyrimidin-5-one, and the addition salts thereof with an acid.

Among the pyrazoline-3,5-dione derivatives that can be

used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in the following patent applications and patents: JP 07-036 159, JP 07-084 348 and US 4 128 425, and in the following publications:

- L. Wyzgowska, Acta. Pol. Pharm. 1982, 39 (1-3), 83.
- E. Hannig, Pharmazie, 1980, 35 (4), 231
- M.H. Elnagdi, Bull. Chem. Soc. Jap., 46 (6), 1830, 1973
- G. Cardillo, Gazz. Chim. Ital. 1966, 96, (8-9), 973,

the teachings of which form an integral part of the present patent application.

Pyrazoline-3,5-dione derivatives that may be mentioned most particularly are:

- 1,2-diphenylpyrazoline-3,5-dione,
- 1,2-diethylpyrazoline-3,5-dione,

and the addition salts thereof with an acid.

Among the pyrrolo[3,2-d]oxazole derivatives that can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in patent application JP 07 325 375, the teaching of which forms an integral part of the present patent application.

Among the pyrazolo[3,4-d]thiazole derivatives that can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in patent application JP 07 244 361 and in J. Heterocycl. Chem. 16, 13, (1979).

Among the thiazoloazole S-oxide and thiazoloazole S,S-dioxide derivatives that can be used as heterocyclic couplers in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of the compounds described in the following documents:

- JP 07 09 84 89;
- Khim. Geterotsilk. Soedin, 1967, p. 93;
- J. Prakt. Chem., 318, 1976, p. 12;
- Indian J. Heterocycl. Chem. 1995, 5 (2), p. 135;
- Acta. Pol. Pharm. 1995, 52 (5), 415;
- Heterocycl. Commun. 1995, 1 (4), 297;
- Arch. Pharm. (Weinheim, Ger.), 1994, 327 (12), 825.

The heterocyclic oxidation dye(s), i.e. the heterocyclic oxidation base(s) and/or the heterocyclic coupler(s) preferably represent(s) from 0.0001% to 12% by weight approximately relative to the total weight of the ready-to-use dye composition, and even more preferably from 0.005% to 6% by weight approximately relative to this weight.

The ready-to-use dye composition in accordance with the invention can also contain, in addition to the heterocyclic oxidation dyes defined above, at least one benzenic oxidation base and/or at least one benzenic coupler and/or at least one direct dye, in particular to modify the shades or to enrich them with glints.

Among the benzenic oxidation bases that may be additionally present in the ready-to-use dye composition in accordance with the invention, mention may be made in particular of para-phenylenediamines,

bis(phenyl)alkylenediamines, ortho-phenylenediamines, para-aminophenols and ortho-aminophenols, and the addition salts thereof with an acid.

When they are used, these benzenic oxidation bases preferably represent from 0.0005% to 12% by weight approximately relative to the total weight of the dye composition, and even more preferably from 0.005% to 6% by weight approximately relative to this weight.

Among the benzenic couplers that may be additionally present in the ready-to-use dye composition in accordance with the invention, mention may be made in particular of meta-phenylenediamines, meta-aminophenols and meta-diphenols, and the addition salts thereof with an acid.

When they are present, these benzenic couplers preferably represent from 0.0001% to 10% by weight approximately relative to the total weight of the ready-to-use dye composition, and even more preferably from 0.005% to 5% by weight approximately relative to this weight.

In general, the addition salts with an acid that can be used in the context of the dye compositions of the invention (oxidation bases and couplers) are chosen in particular from the hydrochlorides, hydrobromides, sulfates, tartrates, lactates and acetates.

The medium that is suitable for dyeing (or support) for the ready-to-use dye composition in accordance with the invention generally consists of water or of a mixture of water and at least one organic solvent to dissolve

the compounds that would not be sufficiently water-soluble.

The pH of the ready-to-use composition in accordance with the invention is chosen such that the enzymatic activity of the laccase is sufficient. It is generally between 4 and 11 approximately, and preferably between 6 and 9 approximately. It can be adjusted to the desired value by means of acidifying or basifying agents usually used in the dyeing of keratin fibers.

The ready-to-use dye composition in accordance with the invention can also contain various adjuvants conventionally used in compositions for dyeing the hair, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures thereof, polymers, antioxidants, enzymes other than the laccases used in accordance with the invention, such as, for example, peroxidases or 2-electron oxidoreductases, penetrating agents, sequestering agents, fragrances, buffers, dispersants, film-forming agents, preserving agents, opacifiers, thickeners and vitamins.

Needless to say, the person skilled in the art will take care to select this or these optionally additional compound(s) such that the advantageous properties intrinsically associated with the ready-to-use dye composition in accordance with the invention are not, or are not substantially, adversely affected by the addition(s) envisaged.

The ready-to-use dye composition in accordance with the invention can be in various forms, such as in the form of liquids, creams or gels, which may be pressurized,

or in any other form that is suitable for dyeing keratin fibers, and in particular human hair. In this case, the heterocyclic oxidation dye(s) and optionally the additional oxidation dye(s) and the laccase-type enzyme(s) are present in the same ready-to-use composition, and consequently said composition should be free of gaseous oxygen, so as to avoid any premature oxidation of the oxidation dye(s).

A subject of the invention is also a process for dyeing keratin fibers, and in particular human keratin fibers such as the hair, using the ready-to-use dye composition as defined above.

According to this process, at least one ready-to-use dye composition as defined above is applied to the fibers for a period that is sufficient to develop the desired coloration, after which the fibers are rinsed, optionally washed with shampoo, rinsed again and dried.

The time required to develop the coloration on the keratin fibers is generally between 3 minutes and 60 minutes and even more specifically between 5 minutes and 40 minutes.

According to one specific embodiment of the invention, the process includes a preliminary step consisting in separately storing, on the one hand, a composition (A) comprising, in a medium that is suitable for dyeing, at least one oxidation dye chosen from the heterocyclic oxidation bases and heterocyclic couplers as defined above, and, on the other hand, a composition (B) comprising, in a medium that is suitable for dyeing, at least one laccase-type enzyme, and then in mixing them

together at the time of use, after which this mixture is applied to the keratin fibers.

Another subject of the invention is a multi-compartment dyeing device or "kit" or any other multi-compartment packaging system, a first compartment of which contains composition (A) as defined above and a second compartment of which contains composition (B) as defined above. These devices may be equipped with a means for applying the desired mixture to the hair, such as the devices described in patent FR-2 586 913 in the name of the Applicant.

The examples that follow are intended to illustrate the invention without thereby limiting its scope.

DYEING EXAMPLE

The following ready-to-use dye compositions were prepared (contents in grams):

COMPOSITION	**1**	**2**
2,4,5,6-Tetraaminopyrimidine sulfate (heterocyclic oxidation base)	0.65	-
para-Phenylenediamine (benzenic oxidation base)	-	0.20
Resorcinol (benzenic coupler)	0.30	-
2-Methoxy-4,5-methylenedioxyaniline monohydrochloride (heterocyclic coupler)	-	0.37
Laccase obtained from Rhus vernicifera at 180 units/mg, sold by the company Sigma	1.8	1.8
Common dye support (*)	(*)	(*)
Demineralized water qs	100 g	100 g

(*): Common dye support:

- Ethanol	20.0 g
- (C_8-C_{10})alkylpolyglucoside as an aqueous solution containing 60% active material (A.M.), sold under the name Oramix CG110® by the company SEPPIC	4.8 g A.M.
- Agent for pH q.s.	pH = 6.5

Each of the ready-to-use dye compositions described above was applied to locks of natural gray hair containing 90% white hairs, for 40 minutes at a temperature of 30°C. The hair was then rinsed, washed with a standard shampoo and then dried.

The hair was dyed in the shades given in the Table below:

EXAMPLE	Shade obtained
1	Coppery mahogany light blond
2	light blond

In the dye compositions described above, the laccase from Rhus vernicifera at 180 units/mg, sold by the company Sigma, can be replaced with 1.0 g of laccase from Pyricularia oryzae at 100 units/mg, sold by the company ICN.

CLAIMS

1. Ready-to-use composition for the oxidation dyeing of keratin fibers, and in particular of human keratin fibers such as the hair, characterized in that it comprises, in a medium that is suitable for dyeing,
- at least one oxidation dye chosen from heterocyclic oxidation bases and heterocyclic couplers, and
- at least one laccase-type enzyme,
said composition being free of heterocyclic coupler chosen from indole, indoline, monocyclic pyridine and phenazine compounds.

2. Composition according to Claim 1, characterized in that the laccase is chosen from laccases of plant, animal or microbial origin or obtained by biotechnology.

3. Composition according to either of Claims 1 and 2, characterized in that the laccase is of plant origin and chosen from the laccases extracted from Anacardiacea plants, from Podocarpacea plants, from Rosmarinus off., from Solanum tuberosum, from Iris sp., from Coffea sp., from Daucus carrota, from Vinca minor, from Persea americana, from Catharanthus roseus, from Musa sp., from Malus pumila, from Gingko biloba, and from Monotropa hypopithys.

4. Composition according to Claim 1 or 2, characterized in that the laccase is of microbial origin or obtained by biotechnology.

5. Composition according to Claim 4, characterized in that the laccase is chosen from laccases of Polyporus versicolor, of Rhizoctonia praticola, of Rhus vernicifera, of Scytalidium, of Polyporus pinsitus, of Myceliophthora thermophila, of Rhizoctonia solani, of Pyricularia oryzae, and variants thereof.

6. Composition according to any one of the preceding claims, characterized in that the amount of laccase(s) is between 0.5 Lacu and 200 Lacu per 100 g of dye composition.

7. Composition according to any one of the preceding claims, characterized in that the heterocyclic oxidation base(s) is(are) chosen from pyrimidine derivatives and pyrazole derivatives, and the addition salts thereof with an acid.

8. Composition according to Claim 7, characterized in that the pyrimidine derivatives are chosen from 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine and pyrazolopyrimidine derivatives, and the addition salts thereof with an acid.

9. Composition according to Claim 8, characterized in that the pyrazolopyrimidine derivatives are chosen from pyrazolo[1,5-a]pyrimidine-3,7-diamine, 2-methylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,5-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, pyrazolo[1,5-a]pyrimidine-3,5-diamine, 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine, 3-amino-

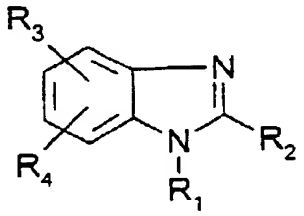
pyrazolo[1,5-a]pyrimidin-7-ol, 3-amino-5-methyl-pyrazolo[1,5-a]pyrimidin-7-ol, 3-aminopyrazolo-[1,5-a]pyrimidin-5-ol, 2-(3-aminopyrazolo[1,5-a]-pyrimidin-7-ylamino)ethanol, 3-amino-7-β-hydroxy-ethylamino-5-methylpyrazolo[1,5-a]pyrimidine, 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol, 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)-(2-hydroxyethyl)amino]ethanol, 2-[(7-aminopyrazolo-[1,5-a]pyrimidin-3-yl)-(2-hydroxyethyl)amino]ethanol, 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine and 2,5,N7,N7-tetramethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, and the addition salts thereof and the tautomeric forms thereof, when a tautomeric equilibrium exists.

10. Composition according to Claim 7, characterized in that the pyrazole derivatives are chosen from 4,5-diaminopyrazole, 4,5-diamino-1-methylpyrazole, 1-benzyl-4,5-diaminopyrazole, 3,4-diaminopyrazole, 1-benzyl-4,5-diamino-3-methylpyrazole, 4-amino-1,3-dimethyl-5-hydrazinopyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-diamino-1-tert-butyl-3-methylpyrazole, 4,5-diamino-3-tert-butyl-1-methylpyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole, 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole, 4,5-diamino-3-hydroxymethyl-1-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole and 4,5-diamino-3-methyl-1-isopropylpyrazole, and the addition salts thereof with an acid.

11. Composition according to any one of the preceding claims, characterized in that the heterocyclic

coupler(s) is(are) chosen from benzimidazole derivatives, benzomorpholine derivatives, sesamol derivatives, pyrazoloazole derivatives, pyrroloazole derivatives, imidazoloazole derivatives, pyrazolopyrimidine derivatives, pyrazoline-3,5-dione derivatives, pyrrolo[3,2-d]oxazoline derivatives, pyrazolo[3,4-d]thiazole derivatives, thiazoloazole S-oxide derivatives and thiazoloazole S,S-dioxide derivatives, and the addition salts thereof with an acid.

12. Composition according to Claim 11, characterized in that the benzimidazole derivatives are chosen from the compounds of formula (I) below, and the addition salts thereof with an acid:



(I)

in which:

R_1 represents a hydrogen atom or a C_1-C_4 alkyl radical,

R_2 represents a hydrogen atom or a C_1-C_4 alkyl or phenyl radical,

R_3 represents a hydroxyl, amino or methoxy radical,

R_4 represents a hydrogen atom or a hydroxyl, methoxy or C_1-C_4 alkyl radical;

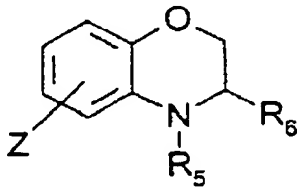
with the proviso that:

- when R_3 denotes an amino radical, then it occupies position 4,
- when R_3 occupies position 4, then R_4 occupies position 7,
- when R_3 occupies position 5, then R_4 occupies

position 6.

13. Composition according to Claim 12, characterized in that the benzimidazole derivatives are chosen from 4-hydroxybenzimidazole, 4-aminobenzimidazole, 4-hydroxy-7-methylbenzimidazole, 4-hydroxy-2-methylbenzimidazole, 1-butyl-4-hydroxybenzimidazole, 4-amino-2-methylbenzimidazole, 5,6-dihydroxybenzimidazole, 5-hydroxy-6-methoxybenzimidazole, 4,7-dihydroxybenzimidazole, 4,7-dihydroxy-1-methylbenzimidazole, 4,7-dimethoxybenzimidazole, 5,6-dihydroxy-1-methylbenzimidazole, 5,6-dihydroxy-2-methylbenzimidazole and 5,6-dimethoxybenzimidazole, and the addition salts thereof with an acid.

14. Composition according to Claim 11, characterized in that the benzomorpholine derivatives are chosen from the compounds of formula (II) below, and the addition salts thereof with an acid:



(II)

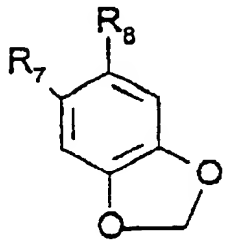
in which:

R_5 and R_6, which may be identical or different, represent a hydrogen atom or a C_1-C_4 alkyl radical,

Z represents a hydroxyl or amino radical.

15. Composition according to Claim 14, characterized in that the benzomorpholine derivatives are chosen from 6-hydroxy-1,4-benzomorpholine, N-methyl-6-hydroxy-1,4-benzomorpholine and 6-amino-1,4-benzomorpholine, and the addition salts thereof with an acid.

16. Composition according to Claim 11, characterized in that the sesamol derivatives are chosen from the compounds of formula (III) below, and the addition salts thereof with an acid:



(III)

in which:

R_7 denotes a hydroxyl, amino, (C_1-C_4)alkylamino, monohydroxy(C_1-C_4)alkylamino or polyhydroxy(C_2-C_4)-alkylamino radical,

R_8 denotes a hydrogen or halogen atom or a C_1-C_4 alkoxy radical.

17. Composition according to Claim 16, characterized in that the sesamol derivatives are chosen from 2-bromo-4,5-methylenedioxyphenol, 2-methoxy-4,5-methylenedioxyaniline and 2-(β-hydroxyethyl)amino-4,5-methylenedioxybenzene, and the addition salts thereof with an acid.

18. Composition according to Claim 11, characterized in that the pyrazoloazole derivatives are chosen from:

- 2-methylpyrazolo[1,5-b]-1,2,4-triazole,
- 2-ethylpyrazolo[1,5-b]-1,2,4-triazole,
- 2-isopropylpyrazolo[1,5-b]-1,2,4-triazole,
- 2-phenylpyrazolo[1,5-b]-1,2,4-triazole,
- 2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole,
- 7-chloro-2,6-dimethylpyrazolo[1,5-b]-1,2,4-tria-

zole,
- 3,6-dimethylpyrazolo[3,2-c]-1,2,4-triazole,
- 6-phenyl-3-methylthiopyrazolo[3,2-c]-1,2,4-triazole,
- 6-aminopyrazolo[1,5-a]benzimidazole,
and the addition salts thereof with an acid.

19. Composition according to Claim 11, characterized in that the pyrroloazole derivatives are chosen from:
- 5-cyano-4-ethoxycarbonyl-8-methylpyrrolo[1,2-b]-1,2,4-triazole,
- 5-cyano-8-methyl-4-phenylpyrrolo[1,2-b]-1,2,4-triazole,
- 7-amido-6-ethoxycarbonylpyrrolo[1,2-a]benzimidazole, and the addition salts thereof with an acid.

20. Composition according to Claim 11, characterized in that the imidazoloazole derivatives are chosen from:
- 7,8-dicyanoimidazolo[3,2-a]imidazole,
- 7,8-dicyano-4-methylimidazolo[3,2-a]imidazole,
and the addition salts thereof with an acid.

21. Composition according to Claim 11, characterized in that the pyrazolopyrimidine derivatives are chosen from:
- pyrazolo[1,5-a]pyrimidin-7-one,
- 2,5-dimethylpyrazolo[1,5-a]pyrimidin-7-one,
- 2-methyl-6-ethoxycarbonylpyrazolo[1,5-a]pyrimidin-7-one,
- 2-methyl-5-methoxymethylpyrazolo[1,5-a]pyrimidin-7-one,

- 2-tert-butyl-5-trifluoromethylpyrazolo[1,5-a]-pyrimidin-7-one,
- 2,7-dimethylpyrazolo[1,5-a]pyrimidin-5-one, and the addition salts thereof with an acid.

22. Composition according to Claim 11, characterized in that the pyrazoline-3,5-dione derivatives are chosen from:
- 1,2-diphenylpyrazoline-3,5-dione,
- 1,2-diethylpyrazoline-3,5-dione,
and the addition salts thereof with an acid.

23. Composition according to any one of the preceding claims, characterized in that the heterocyclic oxidation dye(s) represent(s) from 0.0001% to 12% by weight relative to the total weight of the ready-to-use dye composition.

24. Composition according to Claim 23, characterized in that the heterocyclic oxidation dye(s) represent(s) from 0.005% to 6% by weight relative to the total weight of the ready-to-use dye composition.

25. Composition according to any one of the preceding claims, characterized in that it contains at least one benzenic oxidation base chosen from para-phenylenediamines, bis(phenyl)alkylenediamines, ortho-phenylenediamines, para-aminophenols and ortho-aminophenols, and the addition salts thereof with an acid, and/or at least one benzenic coupler chosen from meta-phenylenediamines, meta-aminophenols and meta-diphenols and the addition salts thereof with an acid, and/or at least one

direct dye.

26. Composition according to any one of the preceding claims, characterized in that the addition salts with an acid are chosen from the hydrochlorides, hydrobromides, sulfates, tartrates, lactates and acetates.

27. Composition according to any one of the preceding claims, characterized in that the medium that is suitable for dyeing consists of water or of a mixture of water and at least one organic solvent.

28. Composition according to any one of the preceding claims, characterized in that it has a pH of between 4 and 11.

29. Process for dyeing keratin fibers, and in particular human keratin fibers such as the hair, characterized in that at least one ready-to-use dye composition as defined in any one of the preceding claims is applied to said fibers, for a period that is sufficient to develop the desired coloration.

30. Process according to Claim 29, characterized in that it includes a preliminary step that consists in separately storing, on the one hand, a composition (A) comprising, in a medium that is suitable for dyeing, at least one heterocyclic oxidation dye as defined in any one of Claims 1, 7 to 24 and 26, and, on the other hand, a composition (B) comprising, in a medium that is suitable for dyeing, at least one laccase-type

enzyme, and then in mixing them together at the time of use, after which this mixture is applied to the keratin fibers.

31. Multi-compartment dyeing device or "kit", characterized in that it includes a first compartment comprising composition (A) as defined in Claim 30 and a second compartment comprising composition (B) as defined in Claim 30.